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(54) **POROUS METAL SUBSTRATE STRUCTURE
FOR A SOLID OXIDE FUEL CELL**

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(75) Inventors: **Chang-Sing Hwang**, Taoyuan County
(TW); **Chun-Huang Tsai**, Taoyuan
County (TW); **Jen-Feng Yu**, Taichung
(TW); **Chun-Liang Chang**, Yunlin
County (TW); **Jun-Meng Lin**, Taipei
(TW); **Shih-Wei Cheng**, New Taipei
(TW)

(58) **Field of Classification Search**
None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,310,611	A *	1/1982	Miskinis	430/111.34
4,958,060	A *	9/1990	Mankins et al.	219/145.22
7,504,172	B2	3/2009	Irvine et al.	
8,241,812	B2 *	8/2012	Hwang et al.	429/463
2010/0098996	A1 *	4/2010	Hwang et al.	429/33
2011/0003235	A1 *	1/2011	Hwang et al.	429/495
2012/0021332	A1 *	1/2012	Hwang et al.	429/486
2014/0051006	A1 *	2/2014	Hwang et al.	429/481

* cited by examiner

Primary Examiner — Vera Katz

(74) *Attorney, Agent, or Firm* — Locke Lord LLP; Tim
Ting kang Xia, Esq.

(73) Assignee: **INSTITUTE OF NUCLEAR
ENERGY RESEARCH ATOMIC
ENERGY COUNCIL, EXECUTIVE
YUAN**, Taoyuan County (TW)

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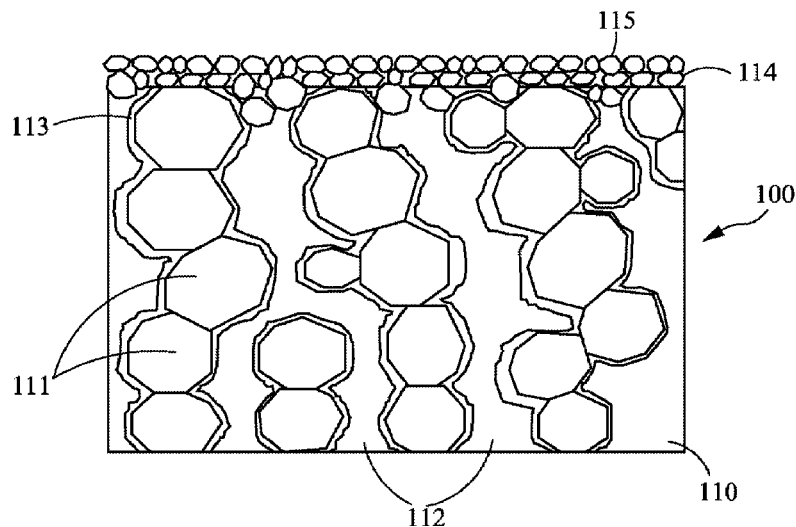
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(2013.01); **C04B 2235/3225** (2013.01); **C04B**

(57) **ABSTRACT**

The disclosure provides a porous metal substrate structure with high gas permeability and redox stability for a SOFC and the fabrication process thereof, the porous metal substrate structure comprising: a porous metal plate composed of first metal particles; and a porous metal film composed of second metal particles and formed on the porous metal plate; wherein the porous metal plate has a thickness more than the porous metal film, and the first metal particle has a size more than the second metal particle. Further, a porous shell containing Fe is formed on the surface of each metal particle by impregnating a solution containing Fe in a high temperature sintering process of reducing or vacuum atmosphere, and the oxidation and reduction processes. The substrate uses the porous shells containing Fe particles to absorb the leakage oxygen.

10 Claims, 5 Drawing Sheets



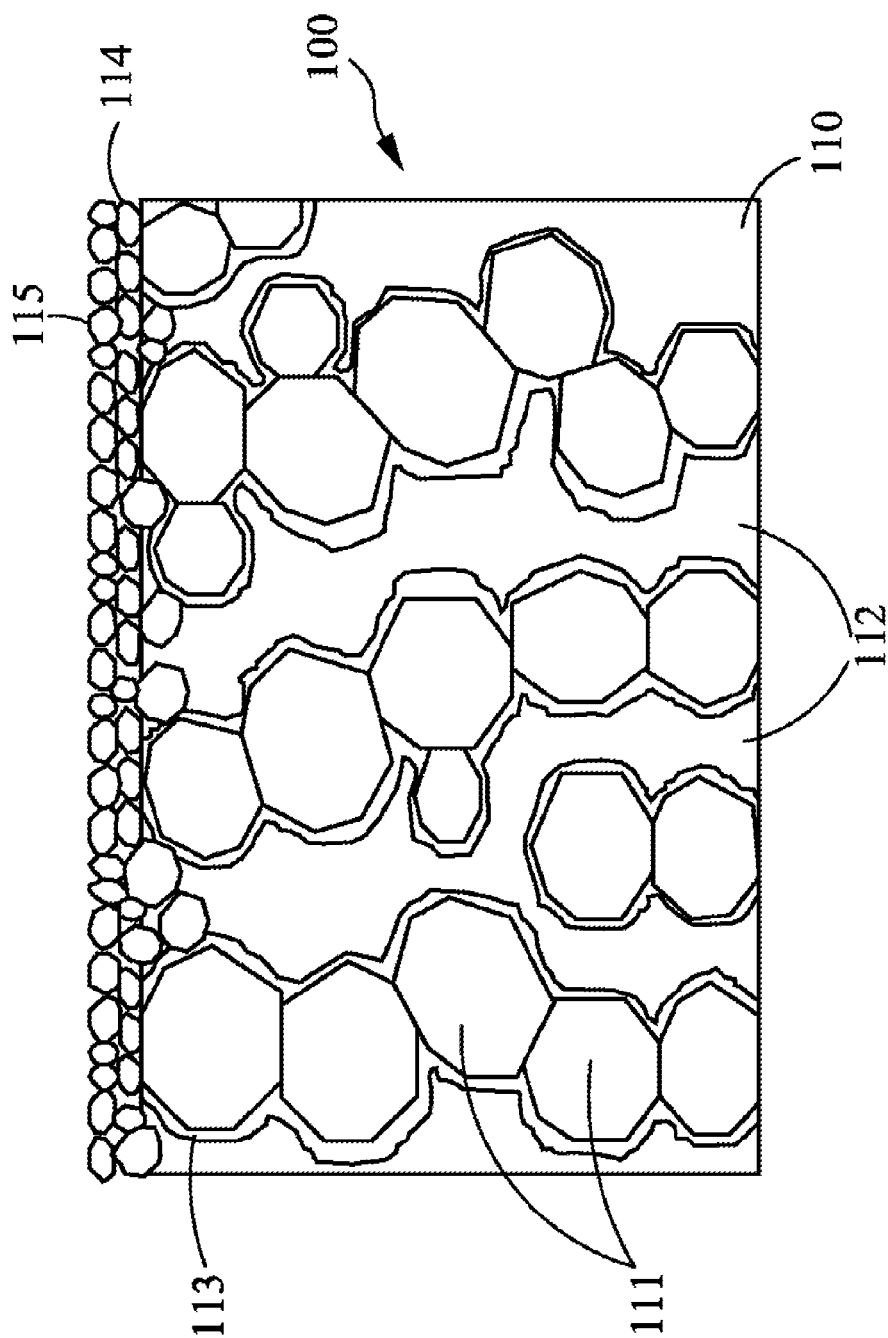


FIG. 1

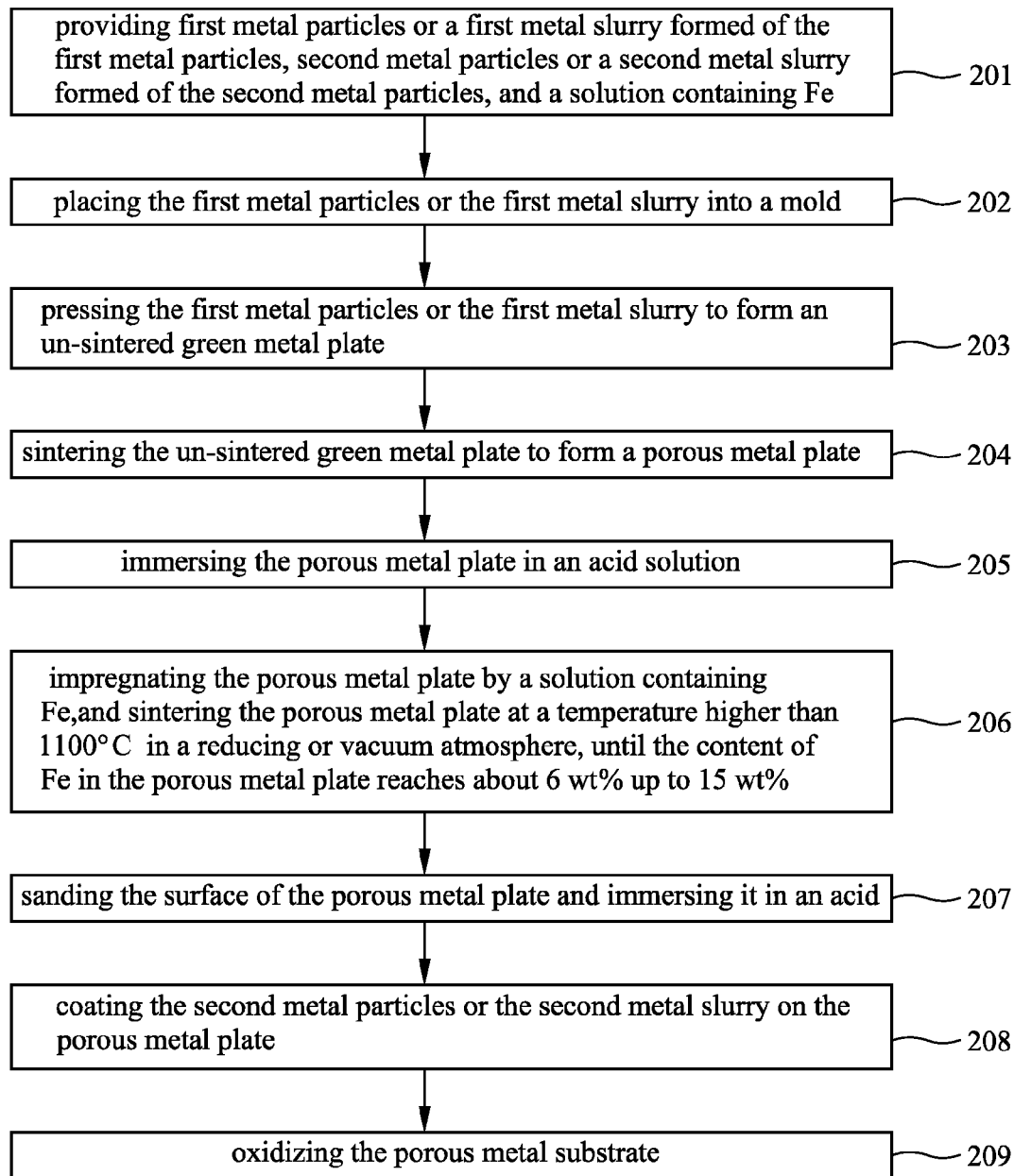


FIG. 2A

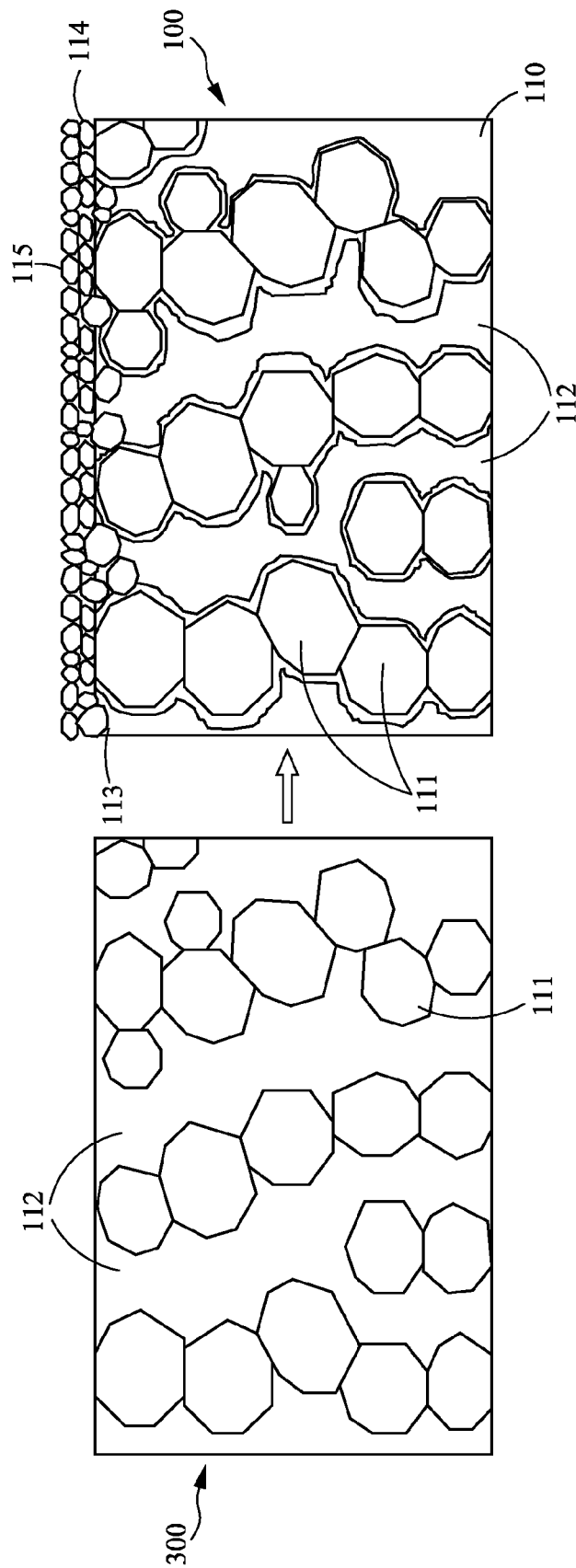


FIG. 2B

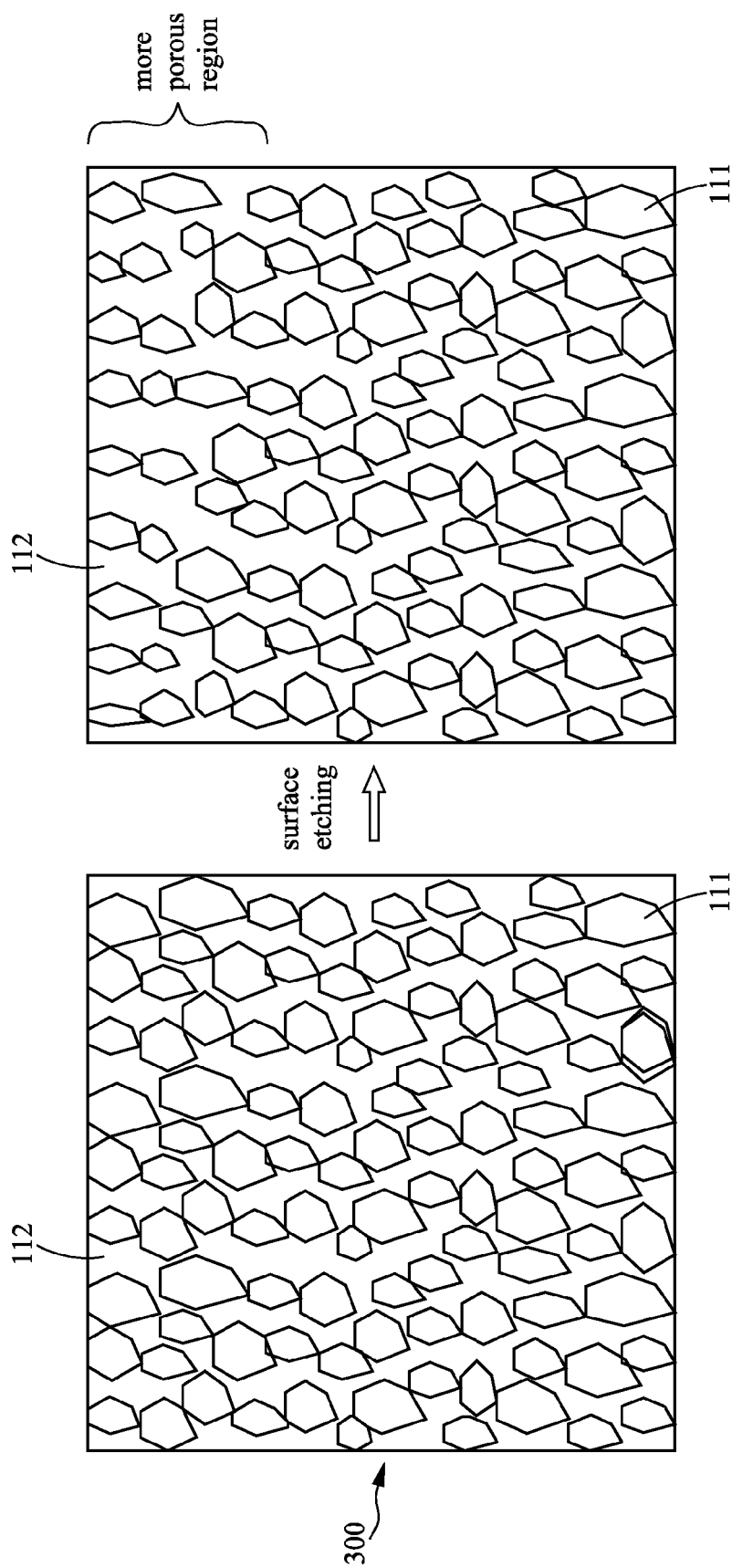


FIG. 2C

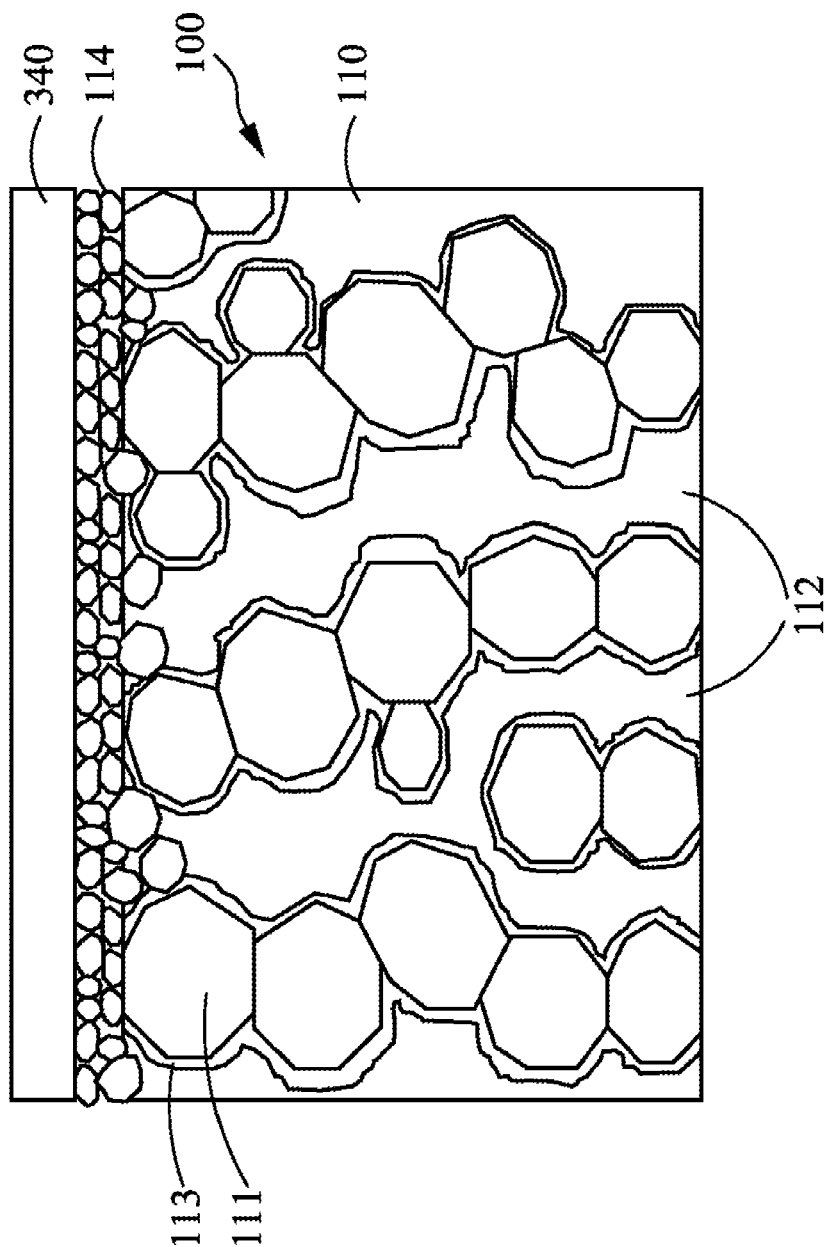


FIG. 3

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POROUS METAL SUBSTRATE STRUCTURE FOR A SOLID OXIDE FUEL CELL

CROSS-REFERENCE TO RELATED APPLICATIONS

This non-provisional application claims priority under 35 U.S.C. §119(a) on Patent Application No. 099124324 filed in Taiwan (R.O.C.) on Jul. 23, 2010, the entire contents of which are hereby incorporated by reference.

TECHNICAL FIELD

The present disclosure relates to a solid oxide fuel cell (SOFC), and more particularly, to a porous metal substrate structure for a SOFC.

TECHNICAL BACKGROUND

Recently the solid oxide fuel cell (SOFC) has been a promising means of converting chemical energy into electrical energy by an electro-chemical mechanism.

Usually in the conventional SOFC, the Yttria Stabilized Zirconia (YSZ) is used as the electrolyte, the cermet composed of nickel (Ni) and YSZ is used as the anode, and the perovskite composed of LaMnO₃ is used as the cathode.

When the SOFC works in a high-temperature environment, the anode fuel, H₂, may somehow be suddenly interrupted, such that the air may get into the anode of the fuel cell. Since Ni, the metal catalyst in the fuel, will be oxidized with its volume increased and its expansion coefficient changed, the anode of the SOFC tends to be broken into pieces.

Consequently, there were ways to promote the redox stability of solid oxide fuel cell. La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ (LSCM) has been proposed as one option for the anode material of the SOFC to have improved anode redox stability. However, the catalytic conversion efficiency of LSCM is less than that of Ni and also LSCM is not a good conductor for oxygen (O) ions, therefore, the polarization resistance of LSCM anode is not low enough.

Moreover, to increase the anode redox stability of a solid oxide fuel cell, it is disclosed that another nickel oxide (NiO) or oxidation barrier (Journal of The Electrochemical Society, 153(10), A1929, 2006) layer is coated on the metal substrate. The NiO particle in this layer has a size less than the NiO particles in the anode, and is to be reduced to a porous Ni layer when the full cell is in normal working conditions. The porous Ni layer tends to be re-oxidized more easily, so as to absorb abnormal oxygen leak to improve redox stability of the anode of a solid oxide fuel cell. However, the permeability of fuel gas decreases accordingly.

In the method mentioned above, the thickness of Ni active layer for improving redox stability of solid oxide fuel cell is smaller than the thickness of the support for solid oxide fuel cell. If the microstructure of the support for solid oxide fuel cell can be modified so that fuel gas (for example, hydrogen) can still pass through the support easily, but the oxygen from leakage can be more effectively absorbed in the longer gas channels of the metal support, then the redox stability improvement will be significantly improved.

TECHNICAL SUMMARY

It is one object of the present invention to provide a porous metal supporting substrate structure with improved gas permeability by acid etching method.

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It is another object of the present invention to provide a porous metal supporting substrate structure with improved anode redox stability for supporting a SOFC.

It is another object of the present invention to provide a porous metal supporting substrate with a surface region that is more porous than the inside of porous metal supporting substrate, hence the stress due to the thermal expansion mismatch between porous metal supporting substrate and the functional layers coated on the porous metal supporting substrate can be reduced to a satisfied level.

It is another object of the present invention to provide a combination of porous metal supporting substrate and a redox stable functional layer coated on the porous metal supporting substrate. This combination provides enhanced stability of anode redox for the SOFC application.

According to one aspect of the present disclosure, one embodiment provides a porous metal substrate structure with high gas permeability and redox stability for a SOFC comprising: a porous metal plate composed of first metal particles; and a porous metal film composed of second metal particles and formed on the porous metal plate; wherein the porous metal plate has a thickness more than the porous metal film, and the first metal particle has a size more than the second metal particle.

According to another aspect of the present disclosure, another embodiment provides a method for fabricating a porous metal substrate structure to support functional layers of a SOFC comprising: providing first metal particles or a first metal slurry formed of the first metal particles, second metal particles or a second metal slurry formed of the second metal particles, and a solution containing Fe, wherein the first metal particle has a size more than the second metal particle; forming a porous metal plate with the first metal particles or the first metal slurry by a sintering process; impregnating the solution containing Fe into the porous metal plate by a vacuum means, and then sintering the impregnated porous metal plate at a temperature higher than 1100° C. in a reducing or vacuum atmosphere, until the content of Fe in the porous metal plate reaches about from 6 wt % to 15 wt %; sanding and acid eroding surface of the porous metal plate; coating the second metal particles on the porous metal plate by a powder covering means or pasting the second metal slurry on the porous metal plate, and then sintering the second metal particles or the dried second metal slurry onto the porous metal plate at a temperature higher than 1100° C. to form a porous metal film on the porous metal plate; forming a porous metal substrate with the Fe impregnated porous metal plate and the porous metal film, and acid eroding the porous metal substrate so as to increase its gas permeability to be larger than 3 Darcy; and oxidizing the porous metal substrate so as to shrink its pore sizes.

Further scope of applicability of the present application will become more apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating exemplary embodiments of the disclosure, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The present disclosure will become more fully understood from the detailed description given herein below and the

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accompanying drawings which are given by way of illustration only, and thus are not limitative of the present disclosure and wherein:

FIG. 1 is a schematic diagram showing the architecture of a porous metal substrate structure for supporting the functional layers of a SOFC according to an embodiment of the present invention.

FIG. 2A is a flowchart of a fabricating method of the porous metal substrate structure for supporting the functional layers of a SOFC according to another embodiment of the present invention.

FIG. 2B is a schematic diagram for comparison between the porous Ni plate and the porous metal substrate for supporting SOFC function layers.

FIG. 2C is the schematic diagram to show a modified porous Ni plate with a more porous surface region before impregnating iron (Fe).

FIG. 3 is a schematic diagram showing a combination of the porous metal supporting substrate and a redox stable functional layer coated on the porous metal supporting substrate according to an exemplary embodiment.

DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

For further understanding and recognizing the fulfilled functions and structural characteristics of the disclosure, several exemplary embodiments cooperating with detailed description are presented as the following.

Please refer to FIG. 1, which is a schematic diagram showing the architecture of a porous metal substrate structure for supporting the functional layer of a SOFC according to an embodiment of the present disclosure. The porous metal substrate **100** is composed of a porous metal plate **110** and a porous metal film **114**, wherein the porous metal plate **110** comprises first metal particles **111**, gas channels **112**, and a porous shell **113**. The first metal particles **111** are composed of a first Ni—Fe mixture. The gas channels **112** are the gaps between the first metal particles **111**, whereby gas is able to permeate through the porous metal substrate **100**. The porous shell **113** is formed on the surface of each of the first metal particles **111**. The porous shell **113** contains a third Ni—Fe mixture, in which the Fe content of the third Ni—Fe mixture is richer than the Fe content of the first Ni—Fe mixture. The porous metal film **114** formed of second metal particles **115** is on the porous metal plate **110**, wherein the second metal particles **115** are composed of Ni or a second Ni—Fe mixture, and the second metal particles **115** are smaller than the first metal particles **111**. The porous shells **113** are capable of absorbing oxygen to have the improved redox stability of SOFC anode. The iron-nickel alloy inside the first metal particles **111** may be capable of improving the mechanic strength of the porous metal plate **110**. Wherein, the porous metal plate **110** has a thickness more than the porous metal film **114**, and the first metal particle **111** has a size more than the second metal particle **115**.

In the other words, the porous metal supporting substrate **100** has the thick porous metal plate **110** and the thin porous metal film **114** on the porous metal plate **110**. The metal particles of the porous metal plate **110** have porous shells **113** on their surfaces. These porous shells **113** containing iron (Fe) and nickel (Ni) particles are capable of absorbing oxygen by the oxidation of iron and nickel particles at fuel cell operation temperatures when there is a loss of hydrogen fuel and a leakage of oxygen into the anode of a solid oxide fuel cell. In addition, the metal particles of the porous metal plate **110**

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contain a mixture of Ni and Fe, so that the mechanic strength of the porous support substrate can be increased.

Referring to FIG. 2A, a flowchart of a fabricating method of the porous metal substrate for supporting the functional layers of a SOFC is schematically shown according to another embodiment of the present disclosure. In Step **201**, first metal particles or a first metal slurry formed of the first metal particles, second metal particles or a second metal slurry formed of the second metal particles, and a solution containing Fe are provided, wherein the first metal particle has a size more than the second metal particle; for example, the first metal particle may have a diameter of about 60 μm to 250 μm . The material of the first metal particles can be nickel, for example. The second metal particle has a diameter of about 20 μm to 60 μm , and the material of the second metal particles can be nickel too. The first and second metal slurries are composed of organic binder, solvent and metal particles, wherein the organic binder can be polyvinyl alcohol or ethyl cellulose and the solvent can be water or α -terpineol. In the embodiment, the first metal particles are larger than the second metal particles. Furthermore, the second metal particles can also be composed of nickel, a Ni—Fe mixture, or a Ni—Co—Fe—Cu mixture. For improving its catalytic performance at high temperature, other metal particles like Pd and Ru can be added therein. The solution containing iron (Fe) is a mixture of alcohol, iron nitrate ($\text{Fe}(\text{NO}_3)_3$) and fine iron oxide (Fe_2O_3 or Fe_3O_4 , for example) particles with size less than 5 μm , or preferably, in a nano-scale size.

In Step **202**, the first metal particles or the first metal slurry is placed into a mold. In the embodiment, the mold is made of graphite and has a depth of from 1.0 mm to 1.5 mm, a length of from 103 mm to 108 mm, and a width of from 103 mm to 108 mm, but is not limited thereby, which can be made of another high-temperature-resistant material. Before the first metal particles or the first metal slurry is placed into the mold, a layer of fine carbon black is coated on the inside surface of the mold to facilitate afterward mold release. In Step **203**, the first metal particles or the first metal slurry being dried in the mold is pressed with a pressure less than 150 MPa to form an un-sintered green metal plate. In Step **204**, the un-sintered green metal plate is vacuum sintered or is sintered in reducing atmosphere or is vacuum hot-press sintered at a temperature larger than 1100° C. for 2 to 6 hours to form a porous metal plate. In the case of using the first metal slurry, the un-sintered green plate obtained from the first metal slurry can also be sintered directly without placing into a mold.

The step **204** is to make a porous nickel metal plate that can be impregnated by the solution containing iron (Fe) in next steps, if the first metal particles are nickel particles. The formed porous nickel metal plate has a thickness in the range from 1 mm to 1.25 mm and an area in the range from 101×101 cm^2 to 103×103 cm^2 .

In Step **205**, the porous metal plate after Step **204** is immersed in an acid solution to increase gas-permeability of the porous nickel metal plate to more than 3 Darcy. In this embodiment, 5% nitric acid (HNO_3) is used to erode the Ni plate, but is not limited thereby. To enhance the erosion rate, the acid solution can be heated to a temperature higher than the room temperature or the acid solution can be placed in an ultrasonic bath. In Step **206**, the porous metal plate after Step **205** is vacuum impregnated by a solution containing iron (Fe). Then the impregnated porous nickel metal plate is sintered at a temperature higher than 1100° C. in a reducing or vacuum atmosphere. This step is repeated until the content of Fe in the porous metal plate reaches about 6 wt % up to 15 wt %.

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In Step 207, the surface of the Fe impregnated porous nickel metal plate is sanded, and is immersed in an acid, for example, in 5% HNO₃. In Step 208, the second metal particles or the second metal slurry is coated on the porous metal plate after Step 207, and then sintered in a reducing or vacuum atmosphere at a temperature of higher than 1100° C. to form a porous nickel metal film on the porous nickel metal plate, if the first and the second metal particles are nickel. The porous nickel metal substrate composed of an iron impregnated porous nickel plate and a porous nickel metal film is then immersed in 5% HNO₃ solution to clean the surface and enhance the permeability of the porous metal substrate. The porous metal film has a thickness less than 100 μm and has surface pores less than 50 μm before oxidation. The second metal particles or the second metal slurry used to form the porous metal film can be Ni particles or Ni—Fe mixture particles with Fe content in the range from 6 to 50 wt %. In the Step 208, the other metal particles composed of Cu, Co, Pd or Ru, or their mixtures thereof can be further added into to form the porous metal film with a better performance of converting hydrocarbon fuel into hydrogen. The coating methods in the Step 208 include powder covering and slurry pasting methods. In Step 209, the porous nickel metal substrate is oxidized at a temperature less than 800° C. in the standard atmosphere for one hour to shrink the surface pores of the porous metal film to less than 35 μm.

After Step 209, to form a porous shell containing Fe on the surfaces of the metal particles in the prepared porous metal substrate, the oxidized porous metal substrate is treated in a reduction atmosphere at a temperature higher than 700° C. The porous shell contains Ni and Fe elements, but Fe elements are rich in the porous shell. After finishing all steps including the reduction process, the porous metal substrate has a gas-permeability of 2 to 5 Darcy.

FIG. 2B is a schematic diagram showing transition from the Ni plate 300 after the Step 204 to the porous metal substrate 100 after the Step 209 and a reduction process. The surface of Ni substrate 300 after the Step 204 can be further etched to be more porous than the inside of Ni substrate 300, as shown in FIG. 2C. The porous region has a depth less than 150 μm and a porosity which is 1.4 to 1.8 times of the inside of porous Ni plate 300. After the surface etching, the steps after Step 205 are continued. By having the more porous region as shown in FIG. 2C, the stress due to the thermal expansion mismatch between the porous metal substrate 300 and any functional layer coated on the porous metal substrate 300 can be further reduced.

An anode functional layer 340 may be further coated on the porous metal substrate 100 to form a combination of the support and the anode functional layer of solid oxide fuel cells. In one exemplary embodiment, a redox stable anode functional layer 340 of LSCM, or Sr_{0.86}Y_{0.08}TiO₃, or La_{0.33}Sr_{0.66}TiO₃ as shown in FIG. 3 is coated on the porous metal substrate 100 by a high-voltage high-enthalpy Ar—He—H₂ atmospheric-pressure plasma spraying process. Here, the anode functional layer 340 provides a resistance for oxygen passing through it and enhances the leakage oxygen to be absorbed by the porous shells (containing iron and nickel particles) of metal particles constructing the porous metal supporting substrate 100 for solid oxide fuel cells. The

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second metal particles of the porous metal film 114 can also have a shell containing iron and nickel particles by the same impregnating, oxidation and reduction processes mentioned above.

With respect to the above description then, it is to be realized that the optimum dimensional relationships for the parts of the disclosure, to include variations in size, materials, shape, form, function and manner of operation, assembly and use, are deemed readily apparent and obvious to one skilled in the art, and all equivalent relationships to those illustrated in the drawings and described in the specification are intended to be encompassed by the present disclosure.

What is claimed is:

1. A porous metal substrate structure with redox stability for a solid oxide fuel cell (SOFC) comprising:
 - a porous metal plate composed of first metal particles after sintering, the first metal particles having a first Fe content of a range from 6 to 15 wt %; and
 - a porous metal film composed of second metal particles after sintering and formed on the porous metal plate; wherein the porous metal plate has a thickness more than the porous metal film;
 and the first metal particles have a size more than the second metal particles,
 - wherein first porous shells are formed on surfaces of the first metal particles, wherein a second Fe content of each of the first porous shells is richer than the first Fe content, and the first porous shells are capable of absorbing leakage oxygen.
2. The porous metal substrate structure of claim 1, wherein the first metal particles are mainly formed of a first Ni-Fe mixture.
3. The porous metal substrate structure of claim 1, wherein the second metal particles are mainly formed of Ni or a second Ni-Fe mixture.
4. The porous metal substrate structure of claim 3, further comprising second porous shells formed of a fourth Ni-Fe mixture and on surfaces of the second metal particles.
5. The porous metal substrate structure of claim 1, wherein the porous metal plate has a thickness of about from 1 to 1.5 mm and has a permeability of from 2 to 5 Darcy.
6. The porous metal substrate structure of claim 1, wherein first metal particles before sintering have a size of from 60 to 250 μm.
7. The porous metal substrate structure of claim 1, wherein the porous metal film has a thickness of less than 100 μm and has surface pores of less than 35 μm after oxidation.
8. The porous metal substrate structure of claim 1, wherein second metal particles before sintering have a size of from 20 to 60 μm.
9. The porous metal substrate structure of claim 1, further comprising a redox stable anode functional layer coated on the porous metal substrate structure by a high-voltage high-enthalpy Ar-He-H₂ atmospheric-pressure plasma spraying process.
10. The porous metal substrate structure of claim 9, wherein the redox stable anode functional layer is formed of a material selected from the group consisting of LSCM, Sr_{0.86}Y_{0.08}TiO₃, and La_{0.33}Sr_{0.66}TiO₃.

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